

Size distribution of acidic sulfate ions in fine ambient particulate matter and assessment of source region effect

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Received 2 March 2003; accepted 7 August 2003

Abstract

Human exposure studies strongly suggested that the fine fraction of ambient particulate matter (PM) and its associated acidic sulfates are closely correlated with observed adverse health effects. Acidic sulfates are the products of atmospheric sulfur dioxide oxidation and neutralization processes.

Few data are available on the amount and size distribution of acidic sulfates within the fine fraction of ambient PM. Knowledge of this distribution will help to understand their toxic mechanisms in the human respiratory tract.

The goals of this research were: (1) to measure the size distribution of hydrogen ion, sulfate, and ammonium within the fine fraction of the ambient aerosol in air masses originating from different source regions; and (2) to examine the effect of the source region and the seasons on the sampled PM composition.

Six size fractions within the fine ambient PM were collected using a micro-orifice impactor. Results from 30 sampling sessions demonstrated that higher total concentrations of these three ions were observed during the warm months than during the cold months of the year. Size distribution results show that the midpoint diameter of the fraction of particles with the largest fraction of hydrogen, sulfate and ammonium ions was $0.38\text{ }\mu\text{m}$. Although most of the mass containing hydrogen and sulfate ions was measured in the fraction of particles with $0.38\text{ }\mu\text{m}$ midpoint diameter, the ultrafine fraction ($<0.1\text{ }\mu\text{m}$) was found to be more acidic. Ambient ion concentrations varied between sampling sessions and seasons, but the overall size distribution profiles are similar.

Air mass back trajectories were used to identify the source region of the sampled aerosols. No apparent source region effect was observed in terms of the distribution profile of the ions. However, samples collected from air masses that originated from, or passed over, high sulfur dioxide emission areas demonstrated higher concentrations of the different ions.

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Keywords: Acidic sulfate ions; Particle size distribution; Ultrafine particles; Sulfur dioxide oxidation; Air mass back trajectory

1. Introduction

Acidic sulfates are major components of atmospheric anthropogenic PM. Acidic sulfates may be either primary or secondary. As primary sulfates, they are emitted directly into the atmosphere as particulate sulfate, sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4). These strongly acidic species readily nucleate and condense to form particulate sulfate. Secondary sulfates are produced in the atmosphere through the gas to

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particle conversion of sulfur dioxide (SO_2) and other sulfur containing gases to form various sulfate species. Acidic sulfates in the atmosphere consist of the strongly acidic H_2SO_4 and ammonium bisulfate (NH_4HSO_4) and the weakly acidic ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). Most of the sulfate in the atmosphere is secondary sulfate (EPA I, 1996; EPA II, 1996). The oxidation of SO_2 into sulfuric acid and sulfate salts takes place via two main mechanisms: (1) a slow gas-phase (homogeneous) oxidation and; (2) a gas/particle phase (heterogeneous) oxidation. The gas/particle phase oxidation is a process which occurs rapidly under high relative humidity (RH) conditions and is particularly rapid in the presence of salts of certain metals (EPA I, 1996; McMurry and Wilson, 1983; Lippmann and Schlesinger, 1979). Sulfuric acid can further react with ambient ammonia (NH_3) to produce (NH_4HSO_4) and the very weakly acidic ($(\text{NH}_4)_2\text{SO}_4$). The proportion of each of the above sulfate species in the atmosphere depends upon meteorological conditions and local concentrations of NH_3 (Lioy and Waldman, 1989; Huntzicker et al., 1980). Since acidic sulfates are mainly secondary pollutants formed through the oxidation processes described above, these pollutants can primarily be found in the fine fraction of the atmospheric aerosols (Koutrakis and Kelly, 1993; Pierson et al., 1989; Tanner et al., 1977; Seinfeld and Pandis, 1998). Fine acidic sulfates tend to persist in the atmosphere and may be transported long distances from their original sources (Rodhe and Grandell, 1981). High acidic sulfates concentrations have been measured not only near SO_2 emission sources, but also at locations far away from the emission sources (Stevens et al., 1980; Huntzicker et al., 1984). Ambient ammonia concentrations decrease with altitude. Therefore, when acidic sulfate particles are emitted above the inversion layer, they can travel long distance without being neutralized by the ammonia rich ground level air (Tanner et al., 1984).

Controlled studies in both humans and animals have demonstrated that exposure to strongly acidic sulfate particles causes an alteration in lung function and particle clearance rates (Amdur et al., 1978; Koenig et al., 1983; Bauer et al., 1988; Leikauf et al., 1984; Schlesinger et al., 1983; Lippmann et al., 1982). However, these effects were not observed following exposure to the weakly acidic ammonium sulfate particles (Schlesinger, 1989; Utell et al., 1982).

Acidic sulfates in the atmosphere consist of the strongly acidic H_2SO_4 and NH_4HSO_4 , and the weakly acidic ($(\text{NH}_4)_2\text{SO}_4$). When ambient aerosol samples are analyzed, the sulfate ion (SO_4^{2-}) that is measured in the sample is the sum of the above three species. Some studies have demonstrated a stronger association between SO_4^{2-} and mortality and morbidity than with any of the other measures of PM, such as total suspended particulate (TSP), PM_{10} (PM with

aerodynamic diameter $\leq 10 \mu\text{m}$) and $\text{PM}_{2.5}$ (PM with aerodynamic diameter $\leq 2.5 \mu\text{m}$) (Ozkaynak and Thurston, 1987; Thurston et al., 1994). As noted above, studies have demonstrated that exposure to strong acidic particles causes an alteration in lung function, while no effect was observed following exposure to (NH_4) $_2\text{SO}_4$ particles. The absence of health effects following exposure to (NH_4) $_2\text{SO}_4$ leads to the hypothesis that the association of SO_4^{2-} with the health effects seen in the epidemiological studies was misleading, and SO_4^{2-} merely served as a surrogate of H^+ which was delivered to the lung by the strongly acidic species (Lippmann, 1989). The above strongly suggests that elevated levels of particle strong acidity (as H^+) content is closely related to adverse health effects of atmospheric PM.

The fine and ultrafine fractions of the atmospheric PM include the primary and secondary acidic sulfates, which are produced through both the homogeneous and heterogeneous processes (Koutrakis and Kelly, 1993; Pierson et al., 1989; Winchester and Bi, 1984; Tanner et al., 1977). Most previous acidic sulfates studies investigated the total PM_{10} or $\text{PM}_{2.5}$ fraction. Therefore, very few data are available on the amount and the size distribution of hydrogen, sulfate and ammonium ions and within the fine and ultrafine fractions (where they are predominantly found) of ambient PM. Knowledge of the size distributions of these species will help in understanding the potential deposition and toxic mechanisms in the human respiratory tract.

Seasonal variability in ambient acidic sulfates concentrations was observed in the past (Spengler et al., 1989; Lioy and Waldman, 1989; Thurston et al., 1994; Malm et al., 1994). However, no information is currently available on whether there is any seasonal effect on the size distribution of acidic sulfates. This research examined this seasonal effect.

It was noted earlier that fine acidic sulfates tend to persist in the atmosphere and may be transported long distances from their original sources. Thus the source region of the fine PM and its precursors may have an effect on the PM composition at distant locations. This study aimed to provide additional information on acidic sulfates exposures by investigating the aerosol composition of air masses originating from different upwind source regions. Using an air mass back trajectory model and a newly developed cluster analysis software, this research also examined the effect of the air mass source region on the sampled PM size distribution and composition.

The goals of this research were to: (1) measure the total mass and the size distribution of hydrogen, sulfate, and ammonium ions within the fine fraction of the ambient PM in air masses originating from different upwind source regions; (2) examine the effect of the source region on the sampled PM composition, and (3) examine the seasonal effect on the PM composition.

2. Experimental design and method

2.1. Sampling location

Ambient sampling was conducted outside the Lanza Laboratory of the Nelson Institute of Environmental Medicine of NYU in Tuxedo, NY. It is a rural site, located approximately 50 mile northwest of New York City, that is free from major industrial and urban pollution sources with relatively clean regional background air. The assumption is that the sampled PM composition is source region dependant. Therefore, air masses originating from different source regions should have distinctly different PM composition at this clean background site.

2.2. Experimental system design

2.2.1. Sampling system for size fractionated particles

The sampling system for size fractionated fine and ultrafine particles is depicted in Fig. 1. This system utilizes annular glass denuders (URG Corp., Carrboro, NC), a micro-orifice impactor (MOI, MSP Corp., Minneapolis, MN) and an Electrostatic Aerosol Sampler (EAS, Model 3100, TSI Inc., St. Paul, MN) for separating and collecting particles within predetermined size fraction ranges. Particles that penetrated the MOI were collected by a filter in parallel with the EAS for subsequent chemical analysis. Only the results from particles collected with the MOI on polycarbonate filters will be presented here. The EAS was used to collect ultrafine particles for a second study and the results of that study were reported separately (Hazi et al., 2001).

2.2.2. Micro-orifice impactor

The MOI used in this study is an eight-stage cascade impactor. The nominal aerodynamic diameter cut points at a flow rate of 30 l/min are 15 (inlet), 3.2, 1.8, 1.0, 0.53, 0.28, 0.16, 0.088, and 0.057 μm . The standard definition for fine particles refers to $\text{PM}_{2.5}$. However, since the size selection of particles in this study was limited by the

manufacturing process of the MOI, size ranges were selected to closely approximate the standard size definitions. In this study, fine fraction will refer to the fraction of particles with diameters smaller than 1.8 μm , and ultrafine fraction will refer to the fraction of particles with diameters smaller than 0.088 μm . Although the focus of this research was the fine and ultrafine fraction of the ambient aerosol (sampled by stages three and below), the first and the second stages were also employed during sampling. These stages with larger cut-sizes were used during sampling to both exclude the coarse, often alkaline, particles which might neutralize the acid collected on the filter and to prevent clogging of the jets of the following stages. In order to collect the entire ultrafine fraction, which was approximated by the cut size of the seventh stage (<0.088 μm), the eighth stage (cut size 0.057 μm) was removed from the impactor and was not used for sampling. Polycarbonate filters 47 mm in diameter and 0.8 μm pore size (Nuclepore Corp., Pleasanton, CA) were used as impaction substrates in the MOI. The same polycarbonate filter was used as the after filter for the collection of particles penetrating the last stage of the MOI.

2.2.3. Diffusion denuders

Acid neutralization by ambient NH_3 and retention of gaseous HNO_3 and SO_2 by sorption or reaction with the filter or the sampled PM are known artifacts of particulate acidity sampling (Appel, 1993). In order to minimize these artifacts during sampling, two sets of annular glass denuders (URG Corp., Carrboro, NC) preceded the MOI's inlet (Fig. 1). Each set contained two identical denuders. The first denuder in each set was coated with citric acid monohydrate and glycerol for the removal of NH_3 from the air stream (Koutrakis et al., 1988). The second denuder in each set was coated with sodium carbonate and glycerol for the removal of gaseous HNO_3 and SO_2 from the air stream (Cheng, 1995). Two sets of denuders were employed in order to increase the gas removal capacity.

2.3. Sample handling

Polycarbonate filters were used as an impaction substrate and after filter in this study. In the laboratory, the filters were loaded into the MOI inside a positive pressure hood supplied with ammonia free and clean scrubbed air (ammonia-free hood). This prevented the introduction of any contaminants on the filters. After the filters were loaded, the MOI was capped and transported to the sampling site.

After a sampling session was completed, the impactor was disconnected from the pump and the denuders and both the inlet and outlet ports were capped. The impactor was then transferred back to the laboratory at the Nelson Institute of Environmental Medicine. In

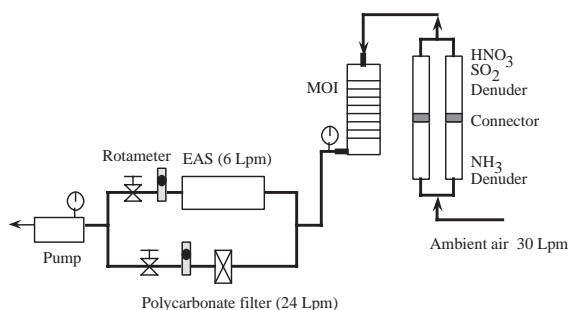


Fig. 1. Sampling system for size fractionated fine and ultrafine particles.

the laboratory, the filters were then removed in the ammonia-free hood and each was stored in a capped 5 ml conical tube. The same tube was later used for extracting the filter. All the capped tubes were stored prior to analysis inside a sealed glass jar that was lined with citric acid coated filter paper. This ensured the protection of the filters from neutralization by NH_3 prior to their analysis.

2.4. Sample analysis

The ion analyses of all the collected samples, together with the field and lab blanks and positive (spiked) controls, involved the application of two methods: (1) the determination of the aerosol strong acidity (H^+) via the pH method developed by Dr. Koutrakis of Harvard School of Public Health (Koutrakis et al., 1988), and (2) the determination of sulfate and ammonium ions by ion chromatography (IC) (Model 4000i, Dionex Corp., Sunnyvale, CA).

2.5. Source region identification

2.5.1. Air mass trajectory calculation

Air mass back trajectories for the sampling days were used to identify the source region of the sampled aerosols in order to evaluate a source–receptor relationship. An air mass trajectory shows the path of an air mass as it is transported through the atmosphere by the wind. Air mass back trajectories were computed according to the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory version 4 (HYSPLIT.4) model available at: <http://www.arl.noaa.gov/ss/models/hysplit.html>. Briefly, in calculating air mass trajectory, the model follows the advection of a particle within an air parcel (Draxler and Hess, 1998). The time integrated advection of the particle is viewed as the simple trajectory of the air parcel. A complete description of this model can be found in the above web site. Two 3-day back trajectories were computed for each sampling day. The trajectories were computed for noon and midnight arrival time and for ground level (10 m) arrival height.

2.5.2. Trajectory cluster analysis

Sampling sessions were carried out over extended time periods varying from 4 to 7 days. Thus there was a large number of trajectories (8–14) per sampling session. In addition, the trajectories would sometimes arrive from a few different upwind directions, and travel at different velocities.

As is evident from the above, there was a need to analyze and compare a large number of trajectories arriving from different upwind directions, and traveling at different velocities. In order to be able to determine

the source region of the majority of the trajectories in each session, the trajectories were categorized into different sets, or clusters, of similar trajectories using cluster analysis.

Trajectory cluster analysis was performed utilizing a newly developed software package that uses the end-point trajectory files generated by the HYSPLIT.4 trajectory program. This software package was developed and made available for this study by Ms. Barbara Stunder of NOAA's ARL in Silver Spring, MD (Stunder, 1996). Cluster analysis is a process which involves two main steps. The first step is grouping the trajectories into well-defined clusters. In this step, the differences among similar trajectories in a cluster are minimized and the differences among clusters are maximized. The second step of cluster analysis is the calculation and plotting of the mean trajectory for each of the clusters. The result is a plot containing one mean trajectory per cluster labeled with the ID number of the cluster and the number of trajectories in that cluster.

3. Results and discussion

A total of 30 sampling sessions were carried out over time periods extending from 4 to 7 days. In order to compare seasonal and temperature effects on the results, the samples were divided into two groups. The first group contained the samples collected during the months of April through September, representing samples collected during the warm months of the year. The second group contained the samples collected during the months of October through March, representing samples collected during the cold months of the year.

3.1. Concentrations of hydrogen, sulfate and ammonium in total mass collected

The mean total ion concentrations for a sampling session was obtained by summing the concentrations measured in the individual size fractions. Concentrations ranged from 13.5 to 73.6 nmol m^{-3} for sulfate, from 23.8 to 139.0 nmol m^{-3} for ammonium and from 1.0 to 18.3 nmol m^{-3} for hydrogen ion.

Fig. 2 shows the mean and standard error (SE) of the total ion concentrations measured for the warm months of the year versus the cold months of the year across all the samples. Student's *t*-test ($\alpha = 0.05$) was used in the comparison of the two groups of samples. It can be seen that significantly higher ambient concentrations of ammonium (p -value = 0.04), sulfate (p -value = 0.01) and hydrogen ion (p -value < 0.01) were measured during the warm months than during the cold months of the year. In both groups, the highest concentrations measured

were of the ammonium ion and the lowest concentrations measured were of the hydrogen ion.

Total ion measurement results are in agreement with other studies (Spengler et al., 1989; Thompson et al., 1991; Thurston et al., 1992; Malm et al., 1994) reporting higher acid and sulfate measurements over the warmer months of the year. Frequently, high acid episodes coincide with high photochemical smog and high ozone levels.

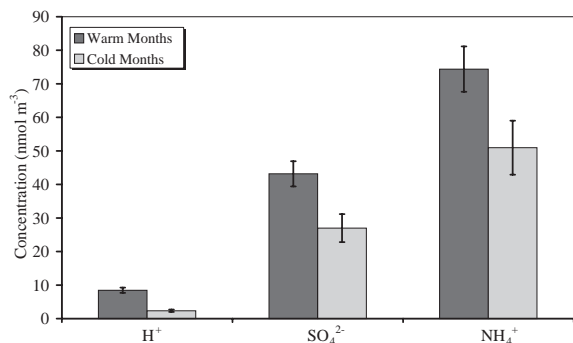


Fig. 2. Total ion concentrations for the warm vs. the cold months of the year (mean \pm SE).

The higher concentrations of the three ions measured during the warm months are caused by the fact that overall, the conditions for SO₂ oxidation processes are more favorable during the warmer months than during the colder months of the year (Lioy and Waldman, 1989; EPA I, 1996). Most of the acidic sulfates in the atmosphere are secondary sulfates formed through the atmospheric oxidation of SO₂. Atmospheric oxidation takes place both by a slow gas phase oxidation and by the faster aqueous phase oxidation. The rapid aqueous phase oxidation takes place within suspended water droplets, non-precipitating clouds and within the liquid film coating the particles (Pandis and Seinfeld, 1989; McMurry et al., 1981; McMurry and Wilson, 1983). Although the atmospheric SO₂ oxidation is not completely understood, the principal oxidation reactions in aqueous phase are thought to be oxidation by ozone, hydrogen peroxide and oxygen (EPA I, 1996; Seinfeld and Pandis, 1998; Lioy and Waldman, 1989; Martin, 1984). The oxidation of SO₂ by oxygen was demonstrated to be catalyzed in the presence of iron and manganese (Lioy and Waldman, 1989; Seinfeld and Pandis, 1998). Although ozone reacts very slowly with SO₂ in the gas phase oxidation, a rapid reaction with SO₂ in the aqueous phase was detailed by several

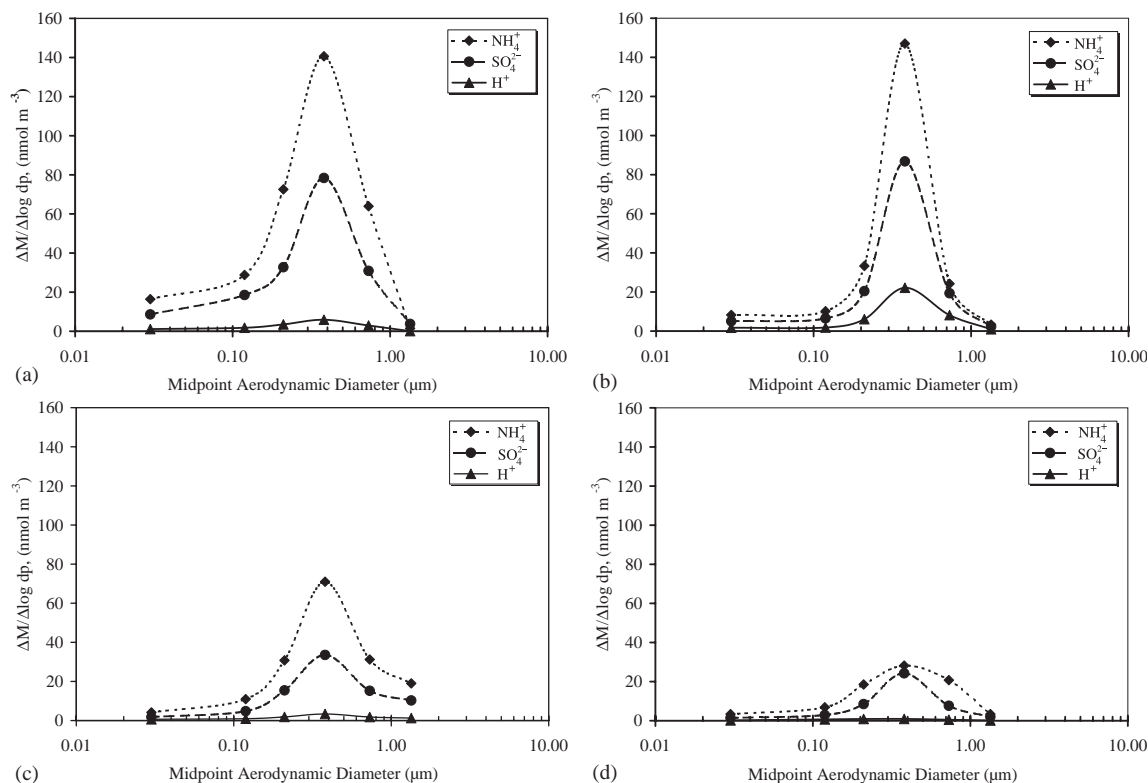


Fig. 3. Size distribution of ion concentrations for sampling sessions conducted during the different seasons: (a) 24/03/98–29/03/98, (b) 08/03/98–08/07/98, (c) 29/09/98–03/10/98, (d) 07/12/98–11/12/98.

investigators (Erickson et al., 1977; Larson et al., 1978; Penkett et al., 1979; Maahs, 1983; Botha et al., 1994). The high effectiveness of H_2O_2 in oxidizing SO_2 in solutions has been demonstrated by several investigators (Hoffman and Edwards, 1975; Penkett et al., 1979; Kunen et al., 1983; McArdle and Hoffman, 1983). From the above one can conclude that atmospheric conditions that lead to an increase in the ambient concentrations of H_2O_2 and O_3 will in turn lead to a higher rate of ambient SO_2 oxidation. Photochemical production of both H_2O_2 and O_3 reaches its peak during the afternoon of summer days. Therefore, higher concentrations of both H_2O_2 and O_3 are measured during the summer than during the winter (Sakugawa et al., 1990) and their concentrations are highest during the afternoon and lowest at night.

Atmospheric humidity is higher during the warm months of the year than during the cold months of the year because the ability of the atmosphere to hold water vapor increases exponentially with temperature. Therefore, the availability of water for aqueous phase oxidation of SO_2 will be higher during the warmer months than during the colder months of the year.

3.2. Concentrations of hydrogen, sulfate and ammonium in individual size fractions

Fig. 3a–d show ion size distribution for four representative samples collected during different seasons. Since each impactor stage collects particles within a given size range, the size distribution results are presented for the midpoint diameter of that size range. The midpoint diameters (in μm) that represent the different size ranges are: 1.34 for 1.8–1.0 μm ; 0.73 for 1.0–0.53 μm ; 0.38 for 0.53–0.28 μm ; 0.21 for 0.28–0.16 μm ; 0.12 for 0.16–0.088 μm ; and 0.03 for particles smaller than 0.088 μm . Ion concentrations were normalized for the particle diameter intervals and are reported in nanomoles per cubic meter. For most samples collected (28 out of 30), the highest ambient sulfate, hydrogen and ammonium ion concentrations were measured at the fraction of particles with 0.38 μm diameter.

Fig. 4 shows the measured mean ion concentrations by size for all the samples collected. The highest mean concentrations of sulfate, hydrogen, and ammonium were measured in the fraction of particles with 0.38 μm diameter. For all size fractions, the highest concentration measured was that of the ammonium ion and the lowest concentration measured was that of the hydrogen ion.

The size distribution of the three ions for the warm months and the cold months is shown in Fig. 5a and b, respectively. The measurements show that except for the magnitude of the concentrations, the distribution profile and the concentration trends are not different.

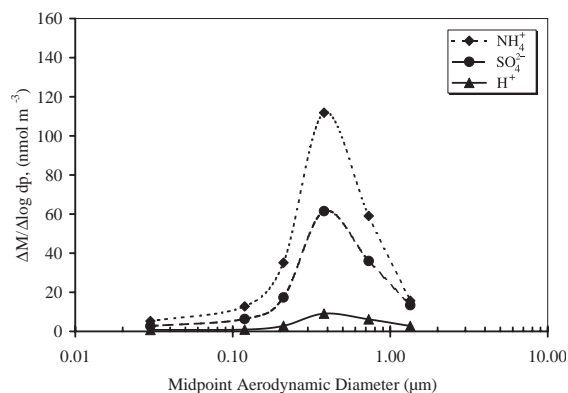


Fig. 4. Size Distribution of mean ion concentrations across all samples.

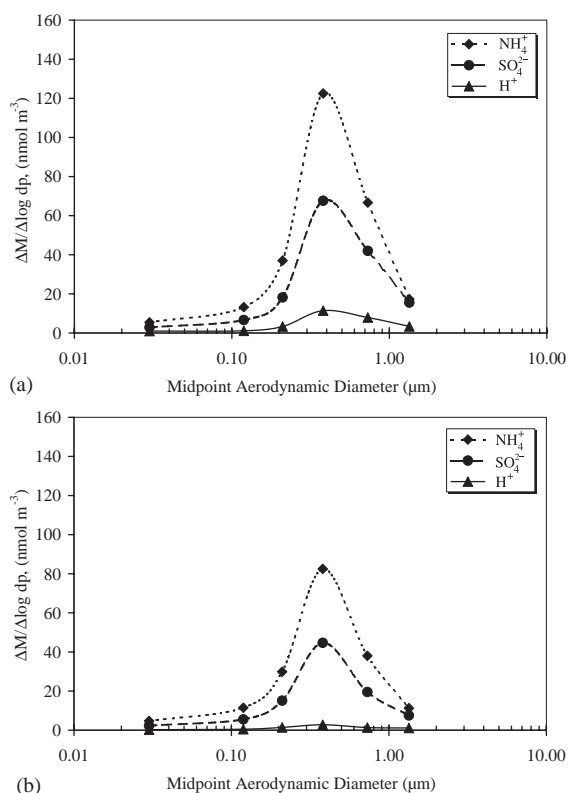


Fig. 5. Size distribution of mean ion concentrations for: (a) the warm months; and (b) the cold months of the year.

Hydrogen to sulfate molar ratio is an index of particle acidity; the higher the ratio, the more acidic is the sulfate species. The highest concentrations of both the hydrogen and the sulfate ions were measured at the size fraction with 0.38 μm diameter. For all the samples, the concentrations of these ions in this fraction were

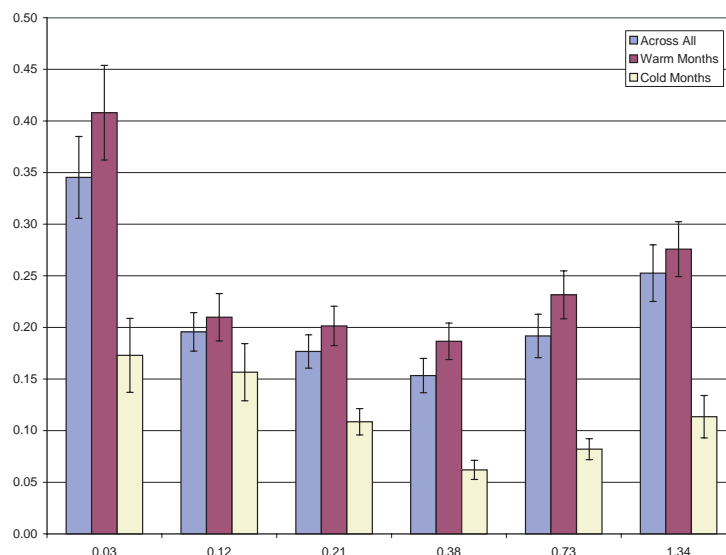


Fig. 6. Hydrogen to sulfate ratio by size across all samples (mean ± SE).

significantly higher than the concentrations measured in the ultrafine fraction ($d < 0.088 \mu\text{m}$). Fig. 6 shows the hydrogen to sulfate molar ratio (mean ± SE) by size across all the samples. This figure demonstrates that although lower in total hydrogen ion, the ultrafine fraction is significantly (non-parametric sign test, $\alpha = 0.05$) more acidic than the $0.38 \mu\text{m}$ diameter fraction. The average hydrogen to sulfate ratio for the ultrafine fraction is the highest while the hydrogen to sulfate ratio for the $0.38 \mu\text{m}$ diameter fraction is the lowest. The hydrogen to sulfate ratio for the ultrafine fraction is essentially double that of the $0.38 \mu\text{m}$ diameter fraction. This finding that ultrafine particles are more acidic than larger particle, was supported by measurements reported by Tanner et al. (1977). Their measurements, obtained at the Brookhaven National Laboratory, also suggested that ultrafine particles are frequently more acidic than the larger particles.

Fig. 7 shows the hydrogen to sulfate molar ratio (mean ± SE) by size for samples collected during the warm months versus samples collected during the cold months of the year. The overall profile of the molar ratio by size of both sets of samples appears to be similar to the profile of the mean across all samples presented in Fig. 6. The main difference is in the magnitude of the ratio. For both sets of samples (Fig. 7) the average ratio for the ultrafine fraction is the highest and the ratio for the $0.38 \mu\text{m}$ midpoint diameter fraction is the lowest. In general, the hydrogen to sulfate ratios for the warm months are higher than those for the cold months for all size fractions. The ultrafine fraction of the group of samples collected during the warm months is almost twice as acidic as the other fractions in that group of samples. The ultrafine fraction of the group of samples

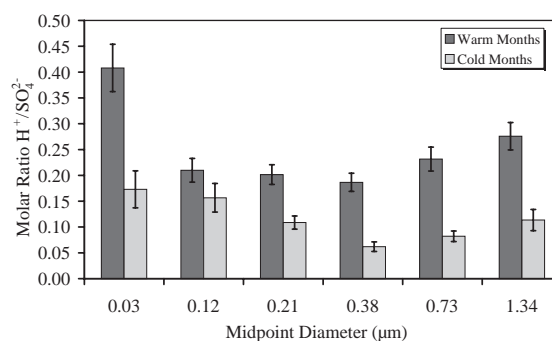


Fig. 7. Hydrogen to sulfate ratio by size for the warm months vs. the cold months (mean ± SE).

collected during the cold months is twice as acidic as the $0.38 \mu\text{m}$ diameter fraction only in that group of samples.

The oxidation of SO_2 into sulfuric acid particles and its subsequent neutralization by ambient ammonia was discussed in detail in previous sections of this work. Ultrafine particles of a few nanometers in diameter are freshly generated particles (EPA I, 1996) and therefore, contain freshly formed acid. As time progresses, and in the presence of ambient ammonia, these particles will be neutralized and grow in diameter by various mechanisms (such as condensation, coagulation) and move into the accumulation mode. The rate of ammonia neutralization varies widely, depending on its emission rate from local sources. Ammonia emission rates, and thus neutralization rates, are high over agricultural areas and cities, and low over forests (Matthews, 1994; Dentener and Crutzen, 1994). Since the sampling site is located in

the middle of a forest, it may be hypothesized that the ultrafine particles sampled at this location are formed locally from local or transported precursors. These particles are sampled before they have sufficient time to interact with ammonia. Therefore, their acidity level will be higher than that of the larger particles, which went through the neutralization and growth processes. In addition, since the conditions for acid formation are more favorable during the warm months, the acidity difference between the two size fractions discussed above (0.38 and $<0.088\mu\text{m}$) will be larger during the warm months than during the cold months.

Particulate H_2SO_4 is the most strongly acidic form of sulfate species that is formed in the atmosphere. Aerosol containing mainly H_2SO_4 particles is indicative of freshly formed sulfate aerosol. H_2SO_4 will react with ambient NH_3 to produce the partly neutralized NH_4HSO_4 . NH_4HSO_4 will further react with NH_3 to produce the completely neutralized $(\text{NH}_4)_2\text{SO}_4$. Therefore, sulfate aerosol containing mainly NH_4HSO_4 can be viewed as a moderately aged aerosol, while sulfate aerosol containing mainly $(\text{NH}_4)_2\text{SO}_4$ can be viewed as a highly aged aerosol. In most size fractions, the concentration of ammonium appears to be almost twice the concentration of sulfate. This concentration of ammonium clearly indicates that the aerosol sampled during the different sessions is mainly aged $(\text{NH}_4)_2\text{SO}_4$ aerosol and also includes some smaller fractions of H_2SO_4 and NH_4HSO_4 .

3.3. Source region effect

It was previously discussed that except for the magnitude of the concentrations of the different ions, the size distribution profile of all of the sampling sessions appears very similar. Therefore it was decided to examine whether air mass source regions have an effect on the total sulfate concentration at this rural site. In order to determine this effect, the trajectories for the sampling sessions with the five highest and five lowest total sulfate concentrations measured were compared. Generally, when comparing air mass back trajectories two major factors should be considered: (1) the region over which the trajectory advected; and (2) the advection velocity of the trajectory. An air mass that stagnates or advects slowly over a high SO_2 emission area will transport higher concentrations of SO_2 oxidation products and precursors. An air mass that advects faster over a high or low SO_2 emission region will transport significantly lower concentrations of SO_2 oxidation products and precursors.

The results of the cluster analysis for the sampling sessions with the five highest and five lowest total sulfate concentrations measured are shown in Fig. 8a and b, respectively. These figures show the mean trajectory for each cluster in that group of sampling sessions. The

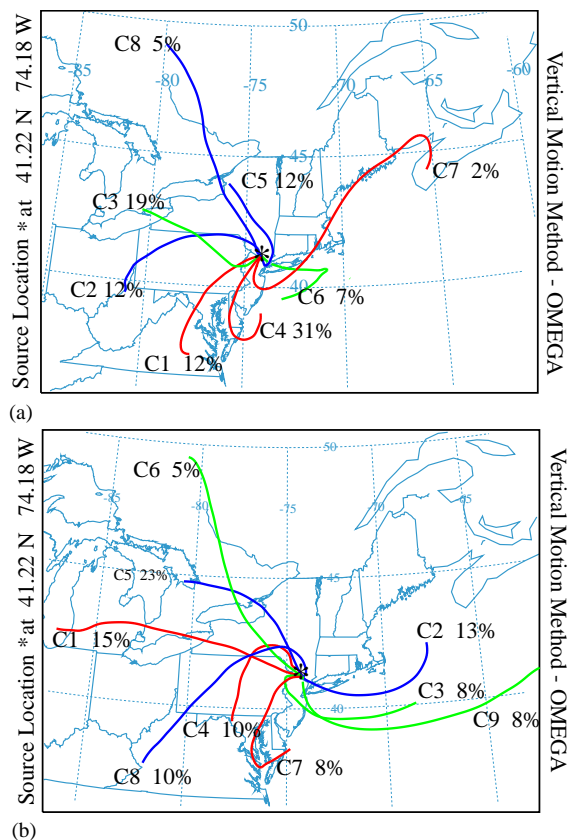


Fig. 8. Mean trajectories for the group of sampling sessions with: (a) the five highest; and (b) the five lowest total sulfate concentrations.

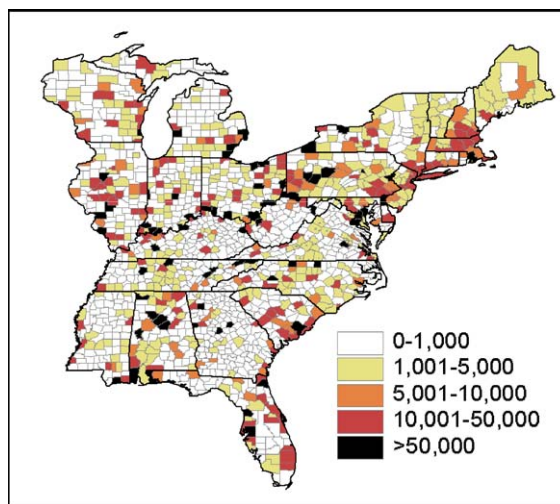


Fig. 9. Sulfur dioxide emissions by county for the eastern half of the US (short tons/year).

mean trajectory of the cluster is labeled with an ID number of the cluster together with the percent of the total trajectories in that cluster. The cluster analysis of the group with the five highest total sulfate concentrations (Fig. 8a) yielded a total of eight mean cluster trajectories (C1–C8). The cluster analysis of the group with the five lowest total sulfate concentrations (Fig. 8b) yielded a total of 9 mean cluster trajectories (C1–C9).

The total yearly SO₂ emission distribution by county for the eastern half of the US is presented in Fig. 9. It clearly shows that the Midwest area, including western Pennsylvania for the purpose of this discussion, and the eastern seaboard south of New York State represent areas with high SO₂ emissions.

The first noticeable difference between the two cluster analyses results (Fig. 8a and b) is the advection velocity of the trajectories. Overall, the trajectories during sampling periods with low SO₄²⁻ concentration (Fig. 8b) appear to be longer than the trajectories during periods with high SO₄²⁻ concentration (Fig. 8a). This indicates a more rapid advection of the air masses during the sampling sessions with the lower sulfate concentrations. The second difference is the percent of total trajectories that traveled over high SO₂ emission areas. During sampling periods with high SO₄²⁻ concentration (Fig. 8a), 75% of the trajectories passed over either the Midwest region or the eastern seaboard south of New York State. As noted above, these areas represent high SO₂ emission areas. During sampling periods with low SO₄²⁻ concentration (Fig. 8b), a smaller fraction (43%) of the trajectories passed over either the Midwest region or the eastern seaboard. In addition, 29% of the trajectories in periods with low SO₄²⁻ concentration (Fig. 8b), both originated and spent most of their advection over the Atlantic Ocean which has no SO₂ sources. In the high SO₄²⁻ concentration periods (Fig. 8a) only 9% of the trajectories originated or traveled over the Atlantic Ocean. These results indicate that the air mass source region does affect the aerosol composition, especially in terms of the total sulfate concentration measured. This effect is evident, despite the fact that sampling sessions were of relatively long duration and, at times, air masses originating from different source regions were sampled during the same session. Although no apparent source region effect was noticed in terms of the distribution profile of the different ions, the effect on the total measured mass of sulfate is clear.

4. Summary and conclusions

This research characterized the fine and ultrafine fractions of the ambient PM in terms of its acidity, sulfate and ammonium size distribution. It is suspected

that these components contribute to the adverse health effects of ambient PM.

A total of 30 sampling sessions were carried out during the four seasons. Results from all sampling sessions demonstrated that significantly higher concentrations of sulfate, hydrogen and ammonium ions were observed during the warm months of the year than during the cold months of the year. Total ion concentrations in the size fraction sampled (<1.8 μm) in nanomoles per cubic meter, for all the fractions sampled ranged from 13.5 to 73.6 for sulfate, from 23.8 to 139.0 for ammonium and from 1.0 to 18.3 for hydrogen ion. The midpoint diameter of the fraction of particles with the largest fractions of sulfate, hydrogen and ammonium was 0.38 μm. Concentrations, in nanomoles per cubic meter, ranged from 6.7 to 31.1 for sulfate, from 0.3 to 7.3 for acid hydrogen and from 7.8 to 68.5 for ammonium for this size fraction. This fraction represents the range of particles diameters from 0.28 to 0.52 μm. Although most of the hydrogen and sulfate mass was found in the 0.28–1.00 μm size range, particles with diameters smaller than 0.088 μm are more acidic. Although ambient concentrations of ions varied between sampling sessions and seasons, the overall distribution profile is similar.

Air mass back trajectories for the sampling days were used to identify the source region of the sampled aerosols. In order to determine the effect of the source region on the aerosol composition, the trajectories for the sampling sessions with the five highest and five lowest total sulfate concentrations measured were compared. No apparent source region effect was observed in terms of the distribution profile of the ions in the different samples. However, samples collected from air masses that originated from or passed over high SO₂ emission areas (such as the Midwest) demonstrated higher concentrations of the different ions.

Certain toxicological studies suggest that atmospheric ultrafine particles are responsible for some of the adverse health effects observed due to exposure to ambient PM. The mechanisms by which ultrafine particles may affect health are far from understood. It is believed that after their deposition in the lung, ultrafine particles can escape alveolar macrophages phagocytosis and enter the pulmonary interstitium (Oberdorster, 2001; Seaton et al. (1995); Nemery, 1990). Hattis et al. (1987, 1990) and Chen et al. (1995) proposed that the number concentration of acidic particles is an important factor in lung toxicity. In addition, Seaton et al. (1995) hypothesize that the number concentration and chemical composition, rather than the mass of particles, account for the observed health effects in the epidemiological studies. It was demonstrated in this work, that the ultrafine fraction is more acidic than the 0.38 μm diameter fraction, which carries most of the hydrogen ion (Figs. 6 and 7). Since over 90% of all airborne

particles are found in the ultrafine size fraction, this implies that at any time, a high number concentration of ultrafine acidic particles is present in the ambient air. These findings provide additional support for the hypotheses proposed by the above investigators. In addition the data derived from this research may assist other scientists in constructing more realistic exposure studies involving both fine and ultrafine PM.

Acknowledgements

We thank Ms. Barbara Stunder of NOAA's ARL for providing us with the trajectory cluster analysis software that was used in this study. We also thank Mr. Paul Peters for his help during the various stages of this work and Ms. Kim Knowlton for her help in generating the SO₂ emission distribution map. This research project was supported by the following grants: US EPA grants # R824791010 and R827351; NIEHS grant # ES00260; NIOSH grant # OH07125; and HEI grant # 98-28.

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